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EXPERIMENTAL AND THEORETICAL STUDIES OF CHEMICAL DYNAMICS AND I--ETC(U)
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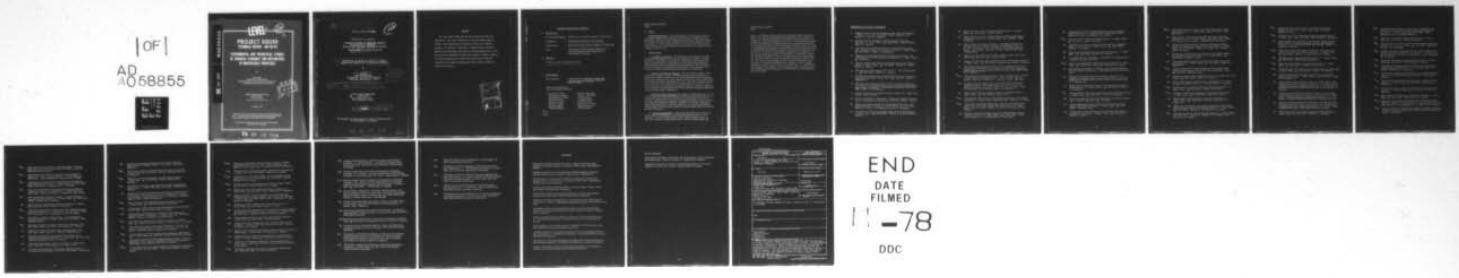

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PROJECT SQUID

TECHNICAL REPORT MIT-90-PU

EXPERIMENTAL AND THEORETICAL STUDIES OF CHEMICAL DYNAMICS AND INSTABILITIES IN IRREVERSIBLE PROCESSES

BY

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AUGUST 1978

Project SQUID is a cooperative program of basic research relating to Jet Propulsion. It is sponsored by the Office of Naval Research and is administered by Purdue University through Contract N00014-75-C1143, NR-098-038.

(14) SQUID-MIT-90-PU

(12)

Technical Report MIT-90-PU

PROJECT SQUID

A COOPERATIVE PROGRAM OF FUNDAMENTAL RESEARCH
AS RELATED TO JET PROPULSION
OFFICE OF NAVAL RESEARCH, DEPARTMENT OF THE NAVY

CONTRACT (15) N00014-75-C-1143 / NR-098-038

(6) EXPERIMENTAL AND THEORETICAL STUDIES OF CHEMICAL DYNAMICS AND INSTABILITIES IN IRREVERSIBLE PROCESSES.

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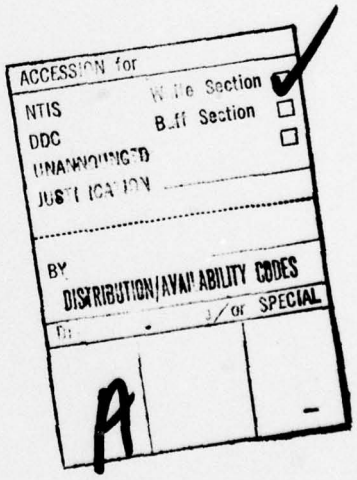
(11) Aug[redacted]978 (12) 70p.

ABSTRACT

The final report summarizes the work accomplished under the subcontract. The overall objectives of the investigation were as follows: The determination of molecular properties of chemical dynamics for reactions of importance to combustion and propulsion. Molecular beam techniques were used for the experimental part of this work and were accompanied by theoretical studies in chemical dynamics. The second purpose was the study of the interaction of chemical reactions with transport processes and flows in gases in which instabilities may occur.



PROJECT SQUID FINAL REPORT

A. Identification

Principal Investigator: John Ross, F. G. Keyes Professor of Chemistry

Contractor: Massachusetts Institute of Technology

Contract No.: Sub 4965-10 under Contract N00014-67-0226-0005

Title: Experimental and Theoretical Studies of Chemical Dynamics and Instabilities in Irreversible Processes

B. Duration:

October 1, 1967 - December 31, 1977

C. Participation

Other Support: Work has been supported in part by the National Science Foundation (30%) and M. I. T. (20%).

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D. Object

Purpose of Research: The determination of molecular properties of chemical dynamics for reactions of importance to combustion and propulsion. Molecular beam techniques were used for the experimental part of this work and were accompanied by theoretical studies in chemical dynamics. The second purpose was the study of the interaction of chemical reactions with transport processes and flows in gases in which instabilities may occur.

E. Achievements

1. Transport Processes: We developed a new method of solving the Boltzmann equation which describes transport processes in dilute gases (47). The method is similar to a WKB-type solution and at any stage of approximation is better than a sonine polynomial expansion. Experimental work was completed on measurements of the viscosity of gases as a function of temperature and pressure. The precision and accuracy of these measurements has not been superceded (54).

2. Theory of Chemical Dynamics: We have made progress in this field along a number of lines. We developed the theory of optical potentials for reactive systems (43, 46); we treated reactions by distorted wave approximations (51), semiclassical analysis (56), direct interaction and complex formation approaches (65, 72). The optical potential method has proven best where applicable for the determination of total collision cross sections. In an analysis of symmetry effects in chemical reactions (67) we derived the theoretical basis of the important Woodward-Hoffmann rules and showed their limitations.

3. Molecular Beam Research: In a number of publications (50, 66, 73, 76) we measured angular distributions of both reactants and products in a chemically reactive system and derived from that total reaction cross sections, probabilities of reactions, threshold conditions, such as activation energy and threshold distances necessary for reaction, and distribution of exothermicity in reaction products. This work contributed to showing that a molecular beam approach yields valuable data not available by other techniques.

4. Chemical Instabilities: Chemical Instabilities occur when nonlinear reaction mechanisms, normally achieved with auto- or cross catalysis, are driven sufficiently far from chemical equilibrium. In that case a number of interesting events, such as multiple stationary

states, oscillations and formation of macroscopic spatial structures may occur. We have made pioneering contributions in a number of areas. We showed the existence of resonance-like phenomena due to boundary or external perturbations (69, 70); we showed the importance of local autocatalysis (71) and predicted new cooperative phenomena in a field of local sites at which autocatalytic reactions may occur (89); we investigated the interaction of mechanical (sound) modes with chemical reactions and showed how chemical reactions may amplify sound waves (75, 79), which is of particular importance in combustion; we have predicted the occurrence of instabilities in illuminated systems (82, 90) and proceeded to confirm our predictions with experiments; we analyzed a variety of waves in oscillatory chemical reactions (80, 93, 101); and we discussed the connection between fluctuations and transitions in chemical instabilities as compared to those in phase transitions. Much of this work is reviewed in Ref. 114. Instabilities and oscillatory phenomena occur in flames and other combustion processes and we believe that we have contributed to an understanding of these phenomena.

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"On the theory of unimolecular reactions: Application of mean first passage time to reaction rates," accepted J. Chem. Phys. (with Itamar Procaccia and Shaul Mukamel).

"A Basis for Orbital Symmetry Rules," accepted Angew. Chemie (with Horia Metiu and George M. Whitesides.

"Statistical Mechanical Theory of the Kinetics of Phase Transitions," accepted Adv. Stat. Mech. (with H. Metiu and K. Kitahara).

"Remarks on Chemical Instabilities," Proceedings of the XVIth Solvay Conference, to appear in Advances in Chemical Physics, Wiley-Interscience, N. Y.

"Instability and Far-from-equilibrium States of Chemically Reacting Systems," to appear in Advances in Chemical Physics, (with P. Hanusse and P. Ortoleva).

"Franck-Condon Factors in Studies of Dynamics of Chemical Reactions. IV. Non-adiabatic Collisions," accepted J. Chem. Phys. (with David J. Zvijac).

"On the efficiency of rate processes," submitted to J. Chem. Phys. (with Dina Gutkowicz-Krusin and Itamar Procaccia).

"Analytic Results for Asymmetric Random Walk with Exponential Transition Probabilities," submitted to J. Stat. Phys. (with Dina Gutkowicz-Krusin and Itamar Procaccia).

"Comment on 'Rate of Polymorphic Transformation Between Phase II and III of Hexachloroethane'," submitted to J. Chem. Soc. (with Horia Metiu)

"Kinetic Instabilities in First Order Phase Transitions," submitted to J. Chem. Phys. (with Ronald Lovett and Peter Ortoleva).

To be submitted:

"The reaction of photo-excited NO_2 with Cyclopropane," to be submitted to J. Chem. Phys. (with N. Presser, H. Petek and G. Eadens).

"Formation of spatial structures in illuminated systems," to be submitted to J. Chem. Phys. (with K. Iwamoto and N. Presser).

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER MIT-90-PU	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) EXPERIMENTAL AND THEORETICAL STUDIES OF CHEMICAL DYNAMIC AND INSTABILITIES IN IRREVERSIBLE PROCESSES		5. TYPE OF REPORT & PERIOD COVERED Final Report 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) John Ross		8. CONTRACT OR GRANT NUMBER(s) N00014-75-C-1143
9. PERFORMING ORGANIZATION NAME AND ADDRESS Chemistry Department Massachusetts Institute of Technology Cambridge, MA 02139		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR-098-038
11. CONTROLLING OFFICE NAME AND ADDRESS Project SQUID Headquaters Chaffee Hall Purdue University, West Lafayette, Indiana 47907		12. REPORT DATE August 1978 13. NUMBER OF PAGES
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) Office of Naval Research, Power Program, Code 473 Department of the Navy 800 No. Quincy St. Arlington, VA 22217		15. SECURITY CLASS. (of this report) Unclassified 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

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17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

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18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Experimental
Chemical Dynamics
Theoretical
Instabilities

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The final report summarizes the work accomplished under the subcontract. The overall objectives of the investigation were as follows: The determination of molecular properties of chemical dynamics for reactions of importance to combustion and propulsion. Molecular beam techniques were used for the experimental part of this work and were accompanied by theoretical studies in chemical dynamics. The second purpose was the study of the interaction of chemical reactions with transport processes and flows in gases in which instabilities may occur.

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S/N 0102-LF-014-6601

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